NATIONAL BUREAU OF STANDARDS

Technical News

BULLETIN

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CONTENTS

COVER: A 100-mg weight is being placed on the sensitive thermobalance used to detect changes in weight of coordination polymer samples as they are heated *in vacuo*. The measurements thus obtained are an indication of polymer thermal stability. (See p. 78)

X-ray Spectrochemical Analysis of Cement

A STUDY of cements by x-ray spectrochemical analysis is being conducted at the Bureau. The purpose of this study,[1] by Leonard Bean, is to determine the feasibility of using x-ray spectrochemical analysis as a routine test method for cement to replace the conventional chemical methods. The results of the work to date show that the x-ray spectrochemical method is potentially suitable for this work, but with present equipment and sample preparation, it does not reduce the overall man-hours required to perform the tests.

The Bureau has been delegated the responsibility for maintaining Federal specifications for portland cement. The Bureau is also responsible for the testing of cement purchased by other government agencies for use in important construction. Because of these responsibilities, and the fact that traditional methods of analyzing cement are both time-consuming and expensive, the Bureau has been working toward revision and updating of methods for chemical analysis. As there are about 175 cement-producing plants in the country, a rapid, low-cost method of analysis is needed that can be used to analyze any cement produced at any plant.

X-ray spectrometers are in use at a number of cement-manufacturing plants for control of raw materials and finished products, but the use of such apparatus for analysis of materials from a single source presents fewer problems than when used on products from a wide variety of compositions. It is this latter requirement that so far has made necessary the time-consuming sample preparation.

A commercial x-ray spectrometer with curved-crystal optics and two types of detectors capable of determining simultaneously the 10 elements of interest in cements was obtained.[2] This apparatus must be calibrated by the use of materials of known chemical composition. The need for a range of such materials, both in this work and in the use of these techniques in industry, led to the preparation and issuance of five new NBS standard samples of cement with a range of composition, to augment the previous standard sample (NBS 177), already available.[3] In addition to the new standard samples, 6 other cements were selected and chemically analyzed. The NBS standard samples were used to prepare the calibration curves. The other 6 cements were treated as unknowns, and their compositions determined by x-ray spectrochemical analysis.

In the conventional methods minor constituents such as titanium, manganese, strontium, and phosphorus are not separated from the major constituents as is the case in the x-ray method. For example, the alumina content obtained by conventional methods also includes titanium dioxide and phosphorus pentoxide. The x-ray method also gives information on minor constituents which are difficult to determine chemically and which may, in the future, be found to play an important part in the performance of cement.

To date it has been possible to obtain the required accuracy only by eliminating the effect of crystalline structure through fusion of the sample with lithium tetraborate and subsequent grinding to a uniform particle size by a special technique. Boric acid is added as a binder to form the pellet used for analysis in the spectrometer. Although only 5 min are required to make the x-ray measurements, the time required to prepare the sample makes the total number of man-hours involved in an analysis roughly the same as that for the conventional chemical methods. New methods of sample preparation are under study; when combined with improved equipment, they may reduce the time factor considerably.

The present study is continuing with the goals of reducing the time required for analysis and of obtaining better accuracy. Efforts will be made to improve instrumentation and to develop sample preparation methods.

[1] *Leonard Bean and Barry W. Mulligan*, X-ray spectrochemical analysis of materials: cement and dental alloys, presented at *ASTM–RILEM symposium, The Impact of Modern Physics on Materials, Feb. 1964.*

[2] *Lithium fluoride crystals and proportional counters were used for calcium, iron, manganese, titanium, and strontium. Ethylenediamine d-tartrate (EDT) crystals and flow Geiger counters were used for phosphorus, silicon, and for aluminum. An ammonium dihydrogen phosphate (ADP) crystal and a flow Geiger counter were used for magnesium. A sodium chloride crystal and a flow Geiger counter were used for sulfur.*

[3] *NBS Standard Samples, 1011, 1013, 1014, 1015, and 1016. For further information on these standards, see NBS Tech. News. Bull.* **46**, 174 (1962). *Standard samples issued by the National Bureau of Standards are described in* Standard Materials, *NBS Mis. Publ. 241 This publication may be ordered for 30 cents from the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., 20402. Up-to-date supplementary inserts are available upon request directly from NBS.*

Accuracy data for six cements: differences between x-ray and chemical values

Cement No.	%CaO	%Fe₂O₃	%Mn₂O	%TiO₂	%SO₃	%SiO₂	%Al₂O₃	%MgO	%SrO
X–1	+0.11	+0.22	−0.04	−0.02	0	+0.24	+0.42	+0.13	0
X–2	+.55	0	+.01	0	0	+.15	+.33	+.08	−.01
X–3	+.24	+.02	−.05	0	−.03	−.17	+.40	+.12	−.01
X–4	+.21	+.01	−.02	−.02	0	+.23	+.42	+.03	+.02
X–5	+.13	−.05	−.03	0	−.01	−.23	0	−.43	−.01
X–6	+.54	+.02	−.04	0	−.01	−.09	+.09	+.10	0
Averaged	+0.30	+0.03	−0.03	−0.00₇	−0.00₈	+0.02	+0.28	+0.00₅	−0.00₂
$\sqrt{\dfrac{\Sigma d^2}{6}}$	(*)	0.09	0.03	0.01	0.01	0.19	(*)	0.20	0.01

*Not reported because of presence of bias.

Mercury 2537-Å Line Isotope Shifts Measured With Unequaled Accuracy

ISOTOPE shifts in the 2537-Å line of mercury now have been measured with an accuracy never attained previously. The NBS measurement [1] involved a selective excitation technique that permits use of interferometers having long path lengths and high resolving power. This technique is an important feature of a recently developed optical method for studying atomic structure. Walter G. Schweitzer, Jr., devised the method in an effort to obtain more accurate data on the hyperfine structure and isotope shifts of the mercury 2537-Å line. With modifications, the procedure could be applied to the study of resonance lines of some other elements.

In the NBS method, interferometric measurements are made on the absorption spectrum of an atomic beam. Because the spectral width of any line from the beam is much less than that of a line from a more conventional source, it is possible to separate structural components that otherwise would overlap extensively. The selective method of excitation—accomplished by means of a source consisting of a single isotope excited in a magnetic field—allows the components to be recorded either one at a time—or at worst—a few at a time.

Mercury is one of the most readily studied elements because it emits sharp, widely separated, bright lines at room temperature and is relatively easy to work with. For these reasons, mercury lines are of considerable interest as length and wavelength standards. A vast amount of time and effort has been expended on the study of the atomic structure of mercury, and especially on the study of the mercury resonance line at 2537-Å. In fact, this line probably has been the subject of more research than any other spectral line. Yet it is only within the last few years that discrepancies among the results of various investigators of the 2537-Å line have begun to converge. Because progress in understanding the 2537-Å line has closely paralleled progress in understanding atomic physics

and spectra in general, new methods for the study of atomic structure frequently are applied initially to the study of this line.

The 2537-Å line is the strongest resonance line—line representing a transition to the ground state—of mercury at a wavelength suitable for experimental investigation. The isotope shifts observed in the line are considered to be due to shifts in the level of the ground state. There may be shifts in the level of the higher state; but, if so, these shifts are very small—of the order of the accuracies of present theories—and may be neglected. Not all the isotope shifts observed in mercry and in other atoms can be explained with present theories. A good test of any new theory would be a comparison with accurate experimental data on one set of isotope shifts for a single state of an atom, such as mercury, which has a large number of isotopes.

The isotope shifts and hyperfine structure of the 2537-Å line are observable only with instruments having high resolving power. A Fabry-Perot interferometer is the best optical instrument for observing complex structure; however, it is difficult to construct a Fabry-Perot interferometer for use in the 2537-Å region. Until very recently, the efficiency of such an interferometer was extremely limited by available materials for the reflective coatings. In addition, the long path lengths required to obtain high resolving power cause the various components to overlap. The problem of resolution can be solved with radiofrequency methods, and these have been applied to the accurate measurement of the hyperfine structure of the 2537-Å line. However, these methods can be applied only indirectly to the measurement of isotope shifts, and in this application do not give as accurate results.

Recently developed optical method used to obtain more accurate data on the hyperfine structure and isotope shifts of the mercury 2537-Å line. The magnetic field applied to the source enables the operator to adjust the wavelength of one of the lines in the source to that of any of the nine components in the absorption spectrum of the atomic beam. Because the signal to the recorder is the difference between the signals received by the two photocells, the recorder gives directly the absorption of the source in the beam. The monochromator isolates the 2537-Å line; the Zeeman filter eliminates the 201b component, except when it is to be observed; and the Hg[198] filter eliminates the 198 component when desired. The interferometer forms the fringe patterns, which are scanned by allowing air to leak slowly and uniformly into the chamber. The air causes a linear change in index of refraction that is equivalent to a linear change in plate separation.
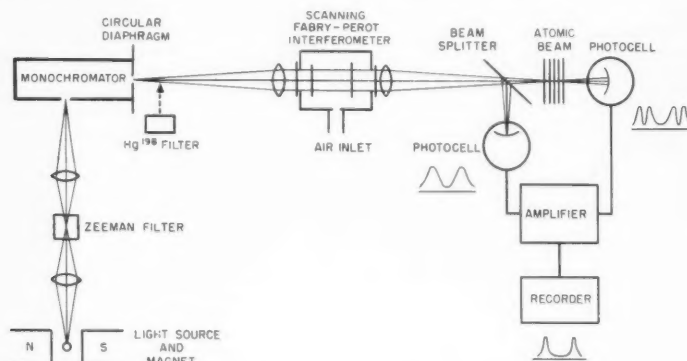
In the study of the mercury 2537-Å line a magnetic field was used to select the desired component for study. The field, applied to the Hg^{198} source, splits the source into three components; two of these can be shifted to the wavelength of any of the nine components in the absorption spectrum of the Hg atomic beam. In this example, the selected component is the Hg^{200} line. The Hg^{198} line can be eliminated with a filter. The applied field is approximately 2300 gauss.

EMISSION COMPONENTS IN Hg^{198} SOURCE

ABSORPTION COMPONENTS IN Hg ATOMIC BEAM
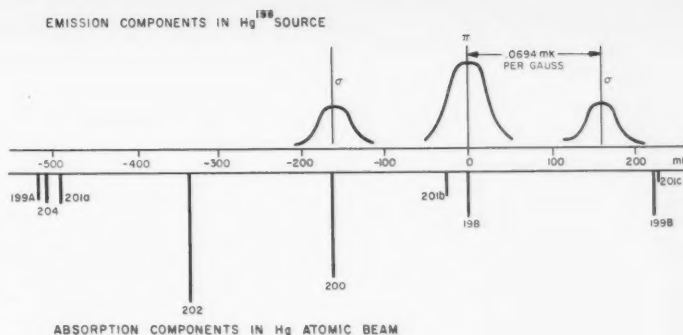
The Bureau method is readily usable to measure both hyperfine structure—structure arising from a nuclear magnetic and mechanical moment—and isotope shifts—structure resulting from the differences in mass or volume of the nuclei of different isotopes—of the same atom. The selective method of excitation is of importance in analyzing elements (such as mercury) which have a large number of isotopes, for it permits the use of interferometers having the desired long path lengths and high resolving powers in which the whole-order difference between two of the line components may be large. Without this selective excitation, the various components of a complex line would overlap when such long spacers are used even if the components themselves were narrow, as is the case with atomic beam sources. The technique is of particular value in studies of elements having resonance lines that fall in the ultraviolet because it circumvents the difficulties usually encountered in obtaining high resolution in this region.

Details of the Method

The NBS apparatus consists of a Hg^{198} light source operated in a magnetic field, a Zeeman filter [2] developed at the Bureau, a monochromator, a Hg^{198} filter, a scanning Fabry-Perot interferometer, and a wavelength-sensitive photoelectric detector. The light from the Hg^{198} source passes into the monochromator (which isolates the 2537-Å line), into the interferometer, and then to a beam splitter. Here the light is split into two parts; one part passes directly to a photomultiplier, while the other passes through an atomic beam of natural mercury before entering a second photomultiplier. The outputs of the two photomultipliers are connected in opposition with the gains so adjusted that no signal is observed as the Fabry-Perot interferometer is scanned with the mercury beam off. Thus, when the mercury beam is on, the signal recorded is the difference signal representing absorption of Hg^{198} in the atomic beam, and the background—often troublesome in absorption experiments—is eliminated.

The fringe pattern formed by the interferometer is scanned by allowing air to leak slowly and uniformly into the interferometer chamber. The resulting linear

change in the index of refraction is equivalent to a linear change in the plate separation.

The magnetic field applied to the Hg^{198} source splits the 2537-Å line into three components: an undisplaced component polarized parallel to the field, and two components which lie symmetrically on either side of the parallel component and are polarized perpendicular to the field. Only those absorption lines in the beam at the same wavelengths as those of the three components in the source can be recorded. The perpendicular components in the source can be shifted to illuminate each of the components of the 2537-Å line in the beam. The parallel component in the source illuminates the Hg^{198} component in the beam. Therefore, by choosing the magnetic field of proper strength, the operator can select each of the nine possible absorption components, singly or in groups of two or three, and they alone will be recorded. Fortunately, the spacing of the absorption components in the beam is such that when the magnetic field is adjusted to cause one of the perpendicular components to coincide with one of the absorption lines, the other perpendicular component will be between lines, resulting in a minimum of interference. Because the Hg^{201b} component interferes with the Hg^{198} component, a Zeeman filter is used to eliminate the 201b component when it is not to be observed. The 198 component can also be eliminated with a filter.

This system makes it possible to record one set of fringes from one component for two or three orders and then to shift quickly (in a time short in comparison with that required to scan an order) to another set of fringes from another component. The fractional-order shift between the two fringe systems can be easily determined by linear interpolation, as there is no overlapping of the two sets. The spacing (relative wavenumber) of each of the components in the beam can be determined in this manner.

[1] For further details, see The hyperfine structure and isotope shifts in the 2537-Å line of mercury by a new interferometric method, by Walter G. Schweitzer, Jr., J. Opt. Soc. Am. 53, No. 9, 1055–1072 (1963).

[2] Zeeman-split absorption lines as very narrow pass filters, by Karl G. Kessler and Walter G. Schweitzer, Jr., J. Opt. Soc. Am. 49, No. 2, 199 (1959).

Polymorphism in Bismuth Oxide

POLYMORPHISM in bismuth oxide and the effect of 33 selected oxide impurities on this polymorphism have recently been investigated at the Bureau by means of high-temperature x-ray diffraction and differential thermal analysis. In the studies on pure bismuth oxide,[1] E. M. Levin and R. S. Roth found two stable and two metastable forms. In the oxide addition portion of the studies,[2] they constructed partial phase diagrams that show the relationships between temperature, composition, and phases present. The results of these investigations have clarified previously conflicting findings and have provided fundamental data on the crystal chemistry of bismuth oxide.

Bismuth oxide (Bi_2O_3) is becoming increasingly important in the ceramics industry as a constituent in high refractive index glasses, in better bonding glazes, and in ceramic materials having special nuclear or electronic applications. To understand its role in ceramic materials, a study of relatively pure Bi_2O_3 is necessary. The Bureau therefore initiated a program to clarify results of previous Bi_2O_3 polymorphism studies and to determine the phase equilibrium relationships.

Studies of Pure Bismuth Oxide

In the investigations of pure bismuth oxide, both reagent grade and spectrographically pure Bi_2O_3 were employed. In general, the polymorphic relationships

in the compound were first deduced from differential thermal analyses of approximately 0.3-g samples. These relationships were then confirmed with data obtained by heating and observing the specimen in a high-temperature x-ray diffractometer furnace.[3]

The results of investigations using these two methods showed that pure Bi_2O_3 possesses two stable (monoclinic and simple or face-centered cubic) and two metastable (tetragonal and body-centered cubic) polymorphs. At 730 ± 5 °C a reversible but not instantaneous transition occurs between the stable high-temperature cubic form and the stable low-temperature monoclinic form. Cooling the cubic form below the 730 °C transition temperature produces either (1) the metastable tetragonal form at 650 °C, or (2) the metastable body-centered cubic (bcc) form at about 640 °C. The body-centered cubic form can be preserved to room temperature, but the tetragonal phase reverts to the stable monoclinic phase between 550 and 450 °C.

Unit cell dimensions, coefficients of linear expansion, and unit cell volumes were calculated for each of the phases. The greatest volume change, a 6.9 percent increase, occurs as the material changes from the monoclinic to the cubic phase. The cubic form shows the greatest coefficient of volume expansion (7.2×10^{-5} per °C).

During these investigations an aging effect on Bi_2O_3 was discovered. Material from a freshly opened bottle of Bi_2O_3 gave an x-ray powder pattern for the pure monoclinic form. About 6 months later, however, material from the same bottle, which had not been desiccated, showed diffraction peaks corresponding to bismutite ($Bi_2O_3 \cdot CO_2$). This discovery led to a group of experiments aimed at accelerating the aging process, and then to some thermal decomposition experiments. In the latter studies, bismutite heated to a temperature of about 400 °C formed tetragonal Bi_2O_3. This form converted to the stable monoclinic form at higher temperature. Studies with bismuth subsalicylate and bismuth subgallate gave similar results.

Studies of Bismuth Oxide With Oxide Impurities

Results from some of the studies with pure Bi_2O_3 conflicted with findings of previous investigators. The
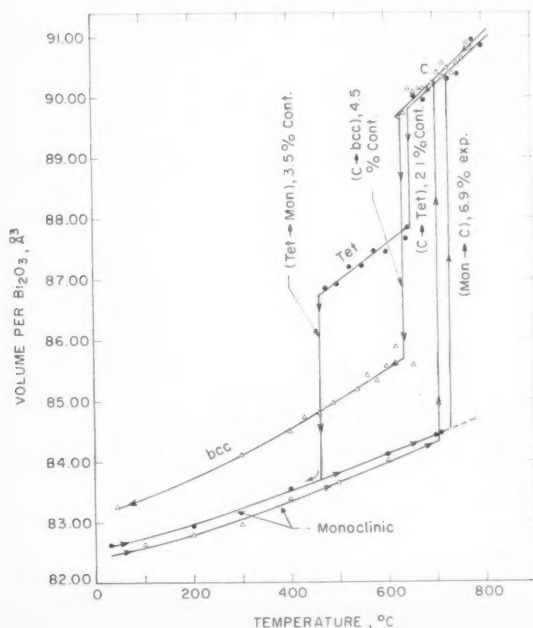
Relationship between temperature and volume per molecule of the polymorphs of reagent grade (●) and spectrographically pure (△) Bi_2O_3. The stable monoclinic form (mon) converts to a stable (simple or face-centered) cubic form (C) at about 730 °C. Upon cooling to approximately 640 °C, the cubic form can convert to the body-centered cubic (bcc) form which can be preserved to room temperature. The cubic form at about 650 °C can also form the tetragonal phase (tet) which converts to the stable monoclinic phase between 450 and 550 °C.
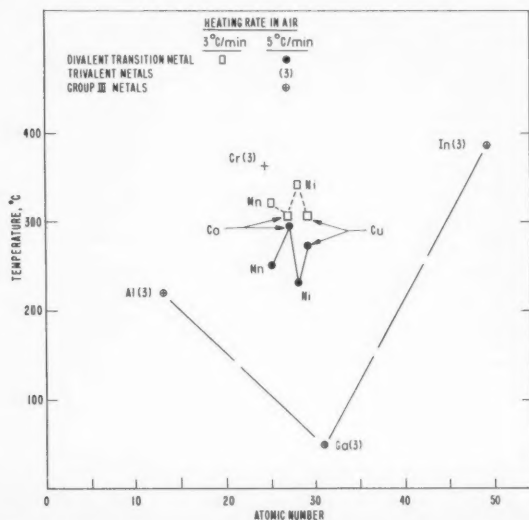
76

	I	II	III	IV	V	VI	VII	VIII		
1	H							He		
2	Li (E)	Be	B (I, E)	C	N	O	F	Ne		
3	Na	Mg (E)	Al (D, E)	Si (C, E)	P (I, SSr)	S	Cl	Ar		
4	K	Ca (Rh, SSr)	Sc	Ti (C)	V (C, SSr)	Cr (C, SSr)	Mn (M, E)	Fe (?, E)	Co	Ni (M, E)
	Cu	Zn (C, E)	Ga (C, E)	Ge (C, E)	As	Se	Br	Kr		
5	Rb (M, E)	Sr (Rh, SSr)	Y	Zr (M, SSr)	Nb (M, SSr)	Mo (SSr)	Tc	Ru	Rh	Pd
	Ag	Cd (M, SSL)	In	Sn (E)	Sb (SSr)	Te (SSr)	I	Xe		
6	Cs	Ba (Rh, SSr)	La (Rh, SSr)	Hf	Ta (SSr)	W (SSr)	Re	Os	Ir	Pt
	Au	Hg	Tl	Pb (I, SSL)	Bi (M)	Po	At	Rn		
Rare Earths 4F	Ce (IV, M, SSr)	Pr	Nd	Pm	Sm (Rh, SSr)	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu (SSr)

Oxides of the elements shown in bold-faced print on this periodic chart were added as impurities to bismuth oxide in polymorphism studies of Bi_2O_3. Those elements in heavy outlines represent oxides that form stable body-centered cubic phases with bismuth oxide. The type of melting is indicated by C—congruent, I—incongruent, and D—decomposes. Further designations used in the chart show some properties of the Bi_2O_3-oxide mixtures: M—metastable body-centered cubic phase, E—eutectic type system, SS_r—solid solution of oxide in Bi_2O_3 with solidus and liquidus raised, SS_L—solid solution with solidus and liquidus lowered, Rh—rhombohedral solid solution phase, and ?—not known.

data indicated that the Bi_2O_3 used in the earlier studies may have been contaminated by unknown oxide impurities. An investigation was therefore initiated to determine the effect of known oxide additions on the polymorphism of bismuth oxide.

Binary combinations, to give an atomic ratio in most cases of 12 Bi to 1 Me (where Me represents the contaminating cation), were prepared from pure Bi_2O_3 and 33 other selected oxides. X-ray diffraction patterns of the oxide mixtures were obtained from room temperature to melting. From these patterns phase diagrams were constructed which showed, in many cases, a bcc phase of variable composition distinct from that of pure Bi_2O_3.

Unit cell calculations for the impure phases showed that the addition of foreign ions to Bi_2O_3 tends to decrease the dimensions of the bcc phase. This decrease is least for the larger impurity ions (such as Mn, Ni, Cd), which tend to form a metastable bcc phase, and greatest for the small impurity ions (such as B, Si, Ge), which tend to form a stable bcc phase. These findings are compatible with theories postulating a cage-type structure in which a central cation, including Bi, is surrounded by a sphere of atoms of the approximate composition $Bi_{12}O_{20}$.

[1] Polymorphism of bismuth sesquioxide, I. Pure Bi_2O_3, by E. M. Levin and R. S. Roth, J. Res. NBS 68A (Phys. and Chem.), No. 2 (Mar.–Apr. 1964).

[2] Polymorphism of bismuth sesquioxide, II. Effect of oxide additions on the polymorphism of Bi_2O_3, by E. M. Levin and R. S. Roth, J. Res. NBS 68A (Phys. and Chem.), No. 2 (Mar.–Apr. 1964).

[3] Improved sample holder for X-ray diffractometer furnace, by E. M. Levin and F. A. Mauer, J. Am. Ceram. Soc. 46, No. 1, 59–60 (Jan. 1963).

IN A RECENT NBS study of the properties of co-ordination polymers, polymers of this type formed by reactions of certain organic molecules with first-row transition metals were investigated. Among the many potential applications for such polymers is the fabrication of missile and rocket components. Results of the study, conducted by Emanuel Horowitz in collaboration with Prof. Theodore P. Perros of the George Washington University (Washington, D.C.), show that the decomposition temperatures of the polymers, and hence their thermal stabilities, are directly related to the atomic numbers of the coordinated metals. This finding has led to a better understanding of the mechanism governing polymer decomposition, and may be of particular use in predicting the thermal behavior of coordinated systems when only a minimum of experimental data is available.[1]

Evaluation of Existing Data

In the assembly and evaluation of some data reported in the literature [2][3] on the thermal stability of metal complexes of 8-hydroxyquinoline, the scientists found that measurements made *in air* often gave contradictory results. For example, when these data were plotted at the Bureau, the graphs indicated that complexes of manganese and nickel were less stable than those of cobalt and copper when the complexes were heated at a rate of 5 °C per minute in air, but that exactly opposite results were obtained when they were heated at the slower rate of 3 °C per minute in air. Moreover, all four complexes apparently had a higher thermal stabil-

The Bureau recently evaluated existing data on the thermal stability of coordination complexes heated *in air* at 3 and 5 °C per minute. This graph shows disparate findings at the two different temperatures for complexes containing divalent transition metals. The graph also shows no apparent relationship among the trivalent oxinates of aluminum (Al), chromium (Cr), gallium (Ga), and indium (In), heated in air.

Thermal Stability &
Cor

ity at the slower rate than at the faster rate (see diagram, at left). Literature data for trivalent oxinates of aluminum, chromium, gallium, and indium heated in air disclosed no apparent connection between the atomic number of the coordinated metals and the temperature at which accelerated weight loss—an indication of thermal stability—occurred.

On the other hand, an evaluation of data [4] on the metal complexes, heated at a rate of about 2.5 °C per minute *in vacuo*, disclosed excellent agreement between their thermal stability and the periodic properties of the central metal. A graph of the atomic number of the metals versus temperature showed that manganese complexes started to lose weight at the highest and those of copper at the lowest temperature (see dia-

Emanuel Horowitz adjusts a control for the tron balance (*right*) during a calibration run used to used at the Bureau to record weight loss in temer calibration, the weight of a sample in the ace the temperature are recorded automatically e ch of a thermogravimetric analysis.

...ty of

...Coordination Polymers

gram, p. 80, left). Cobalt and nickel complexes started to lose weight at temperatures between those of the other two metals. A straight line through these temperatures indicated the close thermal stability-periodicity relationship. In addition, when trivalent oxinates were heated *in vacuo*, it was found that the accelerated weight-loss temperature was essentially the same for all the samples (265 °C), indicating that the thermal stability was independent of the position of the metal in the periodic table.

Experimental Procedure

In the Bureau experiments, divalent manganese, cobalt, nickel, copper, and zinc were combined with the ligand,* *bis*(8-hydroxy-5-quinolyl)methane, both in solution and by thermal polymerization. The coordination polymers thus obtained were highly insoluble colored powders. After they had been purified by repeated extractions, their thermal stability was investigated with a modified electronic thermobalance. Specimens in the 50-mg range were carefully weighed in a platinum crucible which was suspended from the balance beam and positioned in the center of a furnace. The system was sealed and evacuated to about 10^{-3} mm Hg, and then heated from room temperature to 1000 °C at a uniform rate of 2.5 °C per minute. During the entire run, the temperature in the immediate vicinity of the sample and the weight loss were automatically recorded.
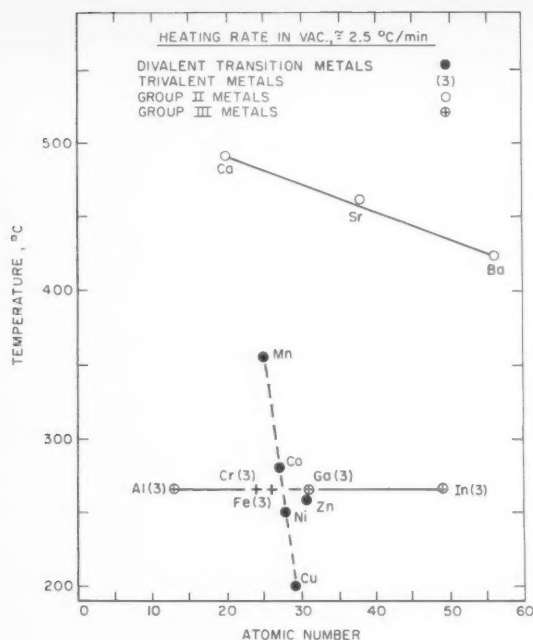
Results

Thermograms expressing weight loss as a function of temperature were made for each polymer and for zinc 8-hydroxyquinolate (zinc oxinate). The thermograms (see diagram, below) showed that a considerable increase in thermal stability was conferred to the co-ordinated systems by the polymerization process. A comparison of the stability of the zinc coordination polymer with that of the zinc oxinate showed that the former began to lose weight at an accelerated rate at a temperature approximately 250 °C above that of the latter. The comparison also showed that at 375 °C the polymer had lost less than 5 percent of its original weight while the oxinate had lost approximately 90 percent.

Quantitative and qualitative analyses of the residue in the platinum crucible after the run indicated that the zinc polymer initially decomposed at the metal-ligand position to give volatile organic fragments and finally metallic zinc or zinc oxide which volatilized at 1000 °C.

...rol for ...tronic thermogravimetric ...ion run ...ed to check the apparatus ...ght loss ...rimental polymers. After ...ple in ...ace (*extreme right*) and ...omatical...e chart during the course

NBS thermograms show weight loss as a function of temperature for five coordination polymers, and for zinc 8-hydroxyquinolate (zinc oxinate). Note that the zinc polymer, much more stable than the zinc oxinate, begins to lose weight at an accelerated rate at a temperature approximately 250 °C above that of the zinc oxinate. In addition, even at 375 °C, the polymer has lost less than 5 percent of its original weight, while zinc oxinate has lost about 90 percent of its original weight.

HEATING RATE IN VAC., ≃ 2.5 °C/min

DIVALENT TRANSITION METALS ●
TRIVALENT METALS (3)
GROUP II METALS ○
GROUP III METALS ⊕

(1) TEMPERATURE AT START OF ACCELERATED WEIGHT
    LOSS.

A. Bis (8-HYDROXY-5-QUINOLYL) METHANE
   CO-ORDINATION POLYMERS

B. 8-HYDROXYQUINOLATES

C. POLYVINYLPHTHALIC ACID METAL POLYMERS
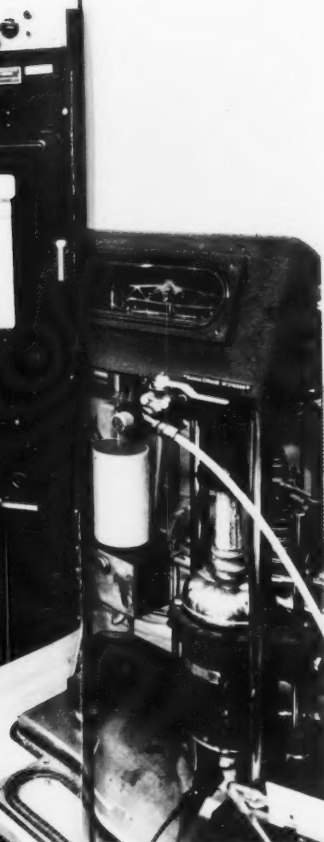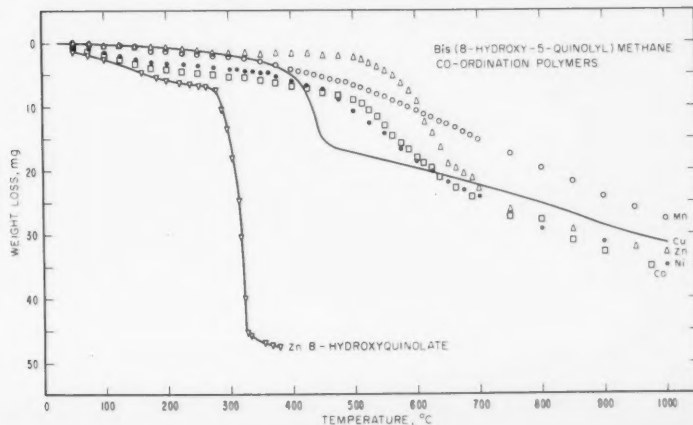
Graph, drawn from evaluated literature data, shows that when coordination complexes are heated *in vacuo* the atomic number of the coordinated metals can be readily correlated with the thermal stability of the complexes.

When the nickel coordination polymer was heated under similar conditions, the residue remaining after the run was within 0.1 percent of the calculated nickel content of the original polymer. Unlike zinc. nickel does not volatilize at 1000 °C.

Evaluation of the decomposition temperatures for all of the coordination polymers showed that their thermal stabilities had the following sequence: manganese> cobalt>nickel>copper<zinc. This sequence is just opposite to that found for the hydrolytic stability of 8-hydroxyquinolates of the first four metals.[5]

The average values for the decomposition temperatures of the coordination polymers were plotted as a function of the atomic number of the central metal atom (see diagram, at right). The resulting plot (curve A) shows that a linear relationship exists between the decomposition temperature of the polymer and the atomic number of the metal in the series: manganese, cobalt, nickel, and copper. The departure of the zinc polymer from the linear relationship may be explained on the basis of the periodic properties of this metal. A similar plot (curve B) representing data taken from the literature on 8-hydroxyquinolates had an almost identical shape, but at considerably lower temperatures. Data taken from the literature[6] for a different coordinated system are also plotted in curve C for comparative purposes.

Coordination polymers containing other *bis*-deriva-
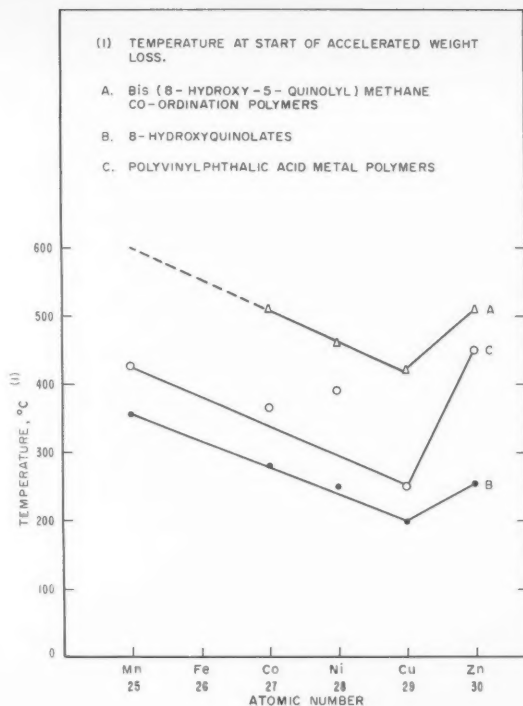
In a Bureau study of coordination polymers formed by reaction of *bis*(8-hydroxy-5-quinolyl)methane with some first-row transition metals, it was found that the thermal stability of the polymers could be directly related to the atomic number of the coordinated metal (curve A). This graph also shows the relationship between the thermal stability and the atomic number of the coordinated metal for the complexes of 8-hydroxyquinolates (curve B) which may be considered as monomer units that are linked together in the polymers through methylene bridges. The data taken from the literature for polyvinylphthalic acid metal polymers, a significantly different coordinated system, are plotted in curve C for comparative purposes.

tives of the 8-hydroxyquinoline ligand are presently being investigated to assess the role played by the ligand as well as by the various metals in promoting high thermal stability. These studies should provide an understanding of the factors governing the physical and chemical properties of coordination polymers, and they may lead to polymeric materials having even better resistance to high temperature than do those investigated in the present work.

A ligand may be considered as an ion or molecule that is bonded to a metal ion in the formation of coordinated complexes.

[1] For further technical details, see Thermal stability of *bis*(8-hydroxy-5-quinolyl) methane coordination polymers, by Emanuel Horowitz and Theodore P. Perros, J. Inorg. Nuclear Chem. **26**, 139–159 (1964).

[2] Inorganic thermogravimetric analysis, by E. Duval, Elsevier Publ. Co., New York (1953).

[3] Analyse thermogravimétrique des principaux oxinates métalliques, by M. Borrel and R. Paris, Anal. Chem. Acta **4**, 267 (1950).

[4] Heat stabilities and volatilities of metal chelates derived from 8-hydroxyquinoline, by R. G. Charles and A. Langer, J. Phys. Chem. **63**, 603 (1959).
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[6] Thermally stable salts of polyvinylphthalic acid, by E. C. Winslow and A. Laferriere, J. Polymer Sci. **60**, 65 (1962).

Computer Sharing Exchange and Service Center Established

A Computer Sharing Exchange and a Computer Service Center have recently been established at the Bureau on an experimental basis. The new facilities were created in response to a request of the Bureau of the Budget, which has found that great savings in both time and money can be realized through computer sharing.

The Sharing Exchange will coordinate requests of Federal Government agencies in the Washington, D.C., metropolitan area for help in locating appropriate computer time and services for their essential work. The Exchange will maintain records of the availability for sharing purposes of the electronic computer facilities of these agencies.

A similar experimental sharing exchange has been operating in Philadelphia, Pa., under Bureau of the Budget sponsorship. Up to now, the presence of the Philadelphia exchange has substantially increased the incidence and value of sharing among government agencies there.

Because the Washington, D.C., area has by far the largest concentration and diversification of computers in the United States, the Bureau has made available its Computation Laboratory as a Service Center in conjunction with the Sharing Exchange. This Center will provide its electronic equipment and personal services at cost to participating agencies to the extent permitted by present equipment and staff provided appropriate arrangements can be made. In addition, it will provide computer programming, problem analysis and formulation, and consultations in these areas. Requests will be considered for business, scientific, engineering, and other types of computer services. Services of the Center will be available either directly or through the Sharing Exchange. Unused time on the computer facilities of the Center will be available to the Exchange for sharing.

The Sharing Exchange and the Service Center will continue in operation for a trial period of 18 to 24 months. Although these facilities are intended to serve Federal Government agencies located in the Washington metropolitan area, their services will not necessarily be barred by distance.

1964 Conference on Radio Meteorology
To Be Held at NBS Boulder Laboratories

A CONFERENCE covering radio meteorology and weather radar, both in general and detailed aspects, will be held September 14–18, 1964, at the NBS Boulder Laboratories. The conference is sponsored by the Inter-Union Committee on Radio-Meteorology (of the International Scientific Radio Union and the International Union of Geodesy and Geophysics), the American Meteorological Society, and the Bureau's Central Radio Propagation Laboratory (CRPL). Organized to strengthen the community of interest among the many specialized fields of radio meteorology, the conference will also serve as the 11th Weather Radar Conference.

The conference will cover the many interactions of radio energy with tropospheric weather conditions. The aspects of tropospheric microwave propagation to be discussed include scatter propagation, ducting, general bending, and attenuation in passing through precipitation, clouds, water vapor, and other gases. The use of radar to observe precipitation, clouds, lightning, and dielectric inhomogeneities of air also will be discussed. Other topics to be considered include microwave radiometry, the changes in the electric field of thunderstorms, and the interactions of radiation from lightning in the troposphere.

The fundamental meteorological processes in which the observed radio phenomena originate will be included among acceptable subjects for papers. Of particular interest, in the light of laser developments, will be papers devoted to interactions involving light waves, particularly coherent and pulsed coherent light. Papers on other topics will be considered if of interest to the specialists attending.

The Radio Meteorology Conference will be organized somewhat differently from the usual conference; the papers accepted will be printed and distributed a month before the conference but will not be presented orally at the conference. Instead, the papers can be examined before the conference by those who plan to attend; they and the author can then discuss the paper on the floor of the conference. The conference committee seeks by this method to encourage the free presentation of ideas and a more effective communication between scientists, leading to constructive discussions of radio-meteorological problems.

A few invited speakers will present review papers and introduce the discussion of new developments reported in the contributed papers. In this way the introduction of new ideas will be as speedy as possible and the relevance, quality, and thoroughness of the discussion enhanced.

Improved Dental Cements

ZINC oxide-eugenol cements have many applications in dentistry. The puttylike coherent mass formed by zinc oxide powder and eugenol liquid is more compatible with both the hard and soft tissues of the mouth than are most dental materials. Hence, it is widely employed by dentists as a base in filling deep tooth cavities and for temporary fillings to ease pain. However, because of its lack of strength, the material sometimes does not resist the biting force transmitted to it through permanent dental restorations.

The Bureau, in a continuing program sponsored by the Federal dental services and the American Dental Association, has therefore been searching for improved dental materials. In the course of this work, Simon Civjan* and Gerhard M. Brauer found that the addition of o-ethoxybenzoic acid (EBA) to a zinc oxide-eugenol mixture improved the physical properties of the mixture. Moreover, its use as a sedative in dental

NBS apparatus for evaluating the shear strength of dental cement specimens. Pins, No. 1, are used to center the 8-mm-long specimen, No. 3, in the U-shaped piece (*top*). To carry out a test, the movable shearing piece, 4 mm wide (No. 4, shown with a fractured specimen) is alined in the slot of the U-shaped device by means of the No. 2 pins, and the specimen is placed in position. The alinement pins are then removed. Double shear is effected by a compressive force applied to the top of the shearing piece with a conventional testing machine that records the load required for specimen fracture. At lower left is shown the mold in which the specimens are prepared.

restorations gave good results.[1] As a consequence of this pilot study, clinical work is being initiated elsewhere to investigate the usefulness of EBA in crown and bridge cements and for orthodontic purposes.

Previous experiments had shown that partial substitution of EBA for eugenol in a zinc oxide-eugenol mixture produced a quick-setting cement with potential dental applications.[2] So in the present study the physical properties of two different types of EBA cements were investigated; these properties were compared with those of zinc oxide-eugenol controls; and the effectiveness of these various formulations in actual tooth restorations was evaluated.
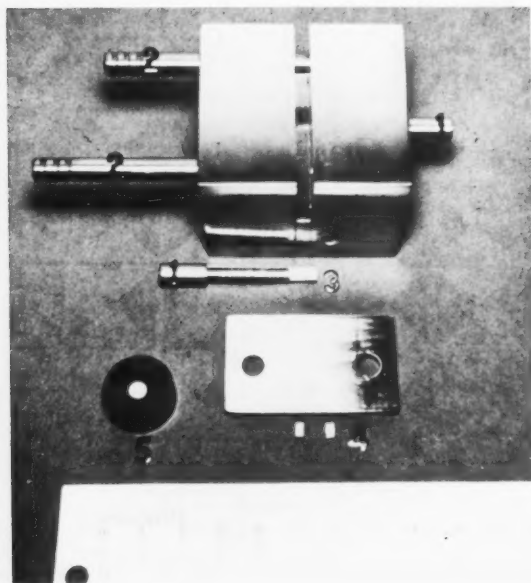
The zinc oxide powders and the eugenol liquids of the controls used in the experiments contained no additives. The powder of one experimental EBA formulation consisted of 90 percent zinc oxide and 10 percent hydrogenated rosin, and that of the other consisted of 74 percent zinc oxide, 6 percent hydrogenated rosin, and 20 percent fused quartz. The same liquid, 62.5 percent EBA and 37.5 percent eugenol, was mixed with both of these powders to make the cements.

Each of the physical properties studied (dimensional stability; density; compressive, tensile, and shear strengths; and solubility and disintegration) was determined by several different methods. The data thus obtained showed good agreement. It was apparent from these data that the EBA cements were superior to the zinc oxide-eugenol controls, and that the cement containing fused quartz had greatly improved properties.

For the evaluation of the various formulations in actual tooth restorations, patients were selected at random and on a voluntary basis as they arrived at an Army dental clinic. In those cases where the controls and the EBA cements were used primarily as temporary fillings, mixed results were obtained. In some types of restorations the controls failed first, and in others the EBA cements failed first. But when the fused-quartz EBA cement was used as pulp-capping media and as sedative bases for permanent tooth restorations, pain was quickly relieved, and the treated teeth remained healthy and nonsymptomatic over observation periods of from 2 to 10 months.

While these results are not conclusive, the laboratory experiments demonstrated that EBA cements have more rapid setting times and better physical properties than has zinc oxide-eugenol cement. In addition, the work showed that fused quartz improves the strength and dimensional stability of EBA cements. The clinical findings, especially with regard to the performance of

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Superior compressive strengths of EBA dental cements
developed at the Bureau. Curve No. 1 is for an EBA
cement containing fused quartz; No. 2, for an EBA ce-
ment without fused quartz; No. 3, for a conventional zinc
oxide-eugenol cement with no additives.

EBA cement when it is used as a sedative, indicate that
this cement will have considerable value in dental
applications.

[1] *For further technical details, see* Clinical behavior of
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(in press), and* Physical properties of cements based on
zinc oxide, hydrogenated rosin, o-ethoxybenzoic acid and
eugenol, *by Simon Civjan and Gerhard M. Brauer, J.
Dental Res.* **43**, No. 2 (Mar.–Apr. 1964).
[2] The reaction of metal oxides with o-ethoxybenzoic acid
and other chelating agents, *by G. M. Brauer, E. E. White,
Jr., and M. G. Moshonas, J. Dental Res.* **37**, 547 (1958);
Improved zinc oxide-eugenol type cements, *by G. M.
Brauer, L. Simon, and L. Sangermano, J. Dental Res.* **41**,
1096 (1962); *and* Cements from metal oxides and chelat-
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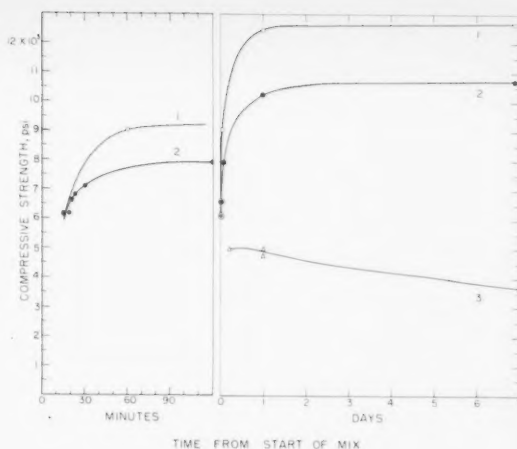
Oxidation Products of
Degraded Plastics Identified

DEGRADATION compounds that form in plastic
building materials during exposure to carbon-arc or
solar radiation have been identified by the Bureau.[1]
To identify these components, V. E. Gray and J. R.
Wright compared the transmission spectra recorded
from solutions of the exposed plastics reacted with
phenylenediamine, with spectra from model carbonyl
compounds treated in the same way. Determining
these degradation products will help chemists to develop
oxidation retardants and to formulate them into the
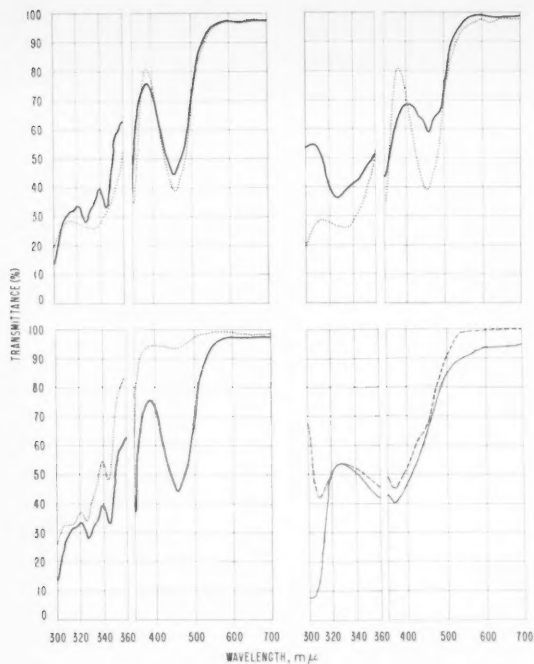plastics, thereby extending the life of these products.

Polymeric materials are relatively new to the build-
ing industry but they offer certain advantages over
other materials. They usually require less structural
support than conventional building materials, need no
painting, and offer a variety of other structural and
decorative properties. In previous studies to evaluate
these materials, the Bureau developed a colorimetric
process[2] to determine the degree of degradation in
plastic building materials exposed to natural or arti-
ficial weathering conditions.

The present investigation is aimed at identifying the
oxidation products formed during the degradation
process. Two plastic materials widely used in the
building industry were selected for the study—poly
(methyl methacrylate) (PMM), and cellulose acetate-
butyrate (CAB).

V. E. Gray places solutions containing samples of plastic
building materials reacted with phenylenediamine into a
transmission spectrometer. The resulting absorbance
peaks are recorded on a strip chart (*right*) and are com-
pared with the spectra of known carbonyl compounds
treated in a similar manner.

To obtain the spectra of the photodegraded plastic,
1-g specimens of exposed PMM or CAB were dis-
solved in glacial acetic acid. This solution, when
added to a solution of a phenylenediamine, produced
a pronounced color indicating the presence of oxida-
tion products. A solution of unexposed plastic, of the
same concentration in glacial acetic acid, was prepared
and used in the reference beam. The absorbance
values at the maxima obtained from solutions of ex-
posed plastic mixed with diamine were corrected by
subtracting any absorbance values of the solution of un-

tral range considerably different than that of the exposed specimens. The spectra of those compounds that became colored in diamine and did produce absorbance peaks in the 300 to 700 mμ range were compared with the spectra of the exposed materials. Although it is not possible to rule out the presence of some other compounds. a mixture of α-keto acids, glyoxal, and pyruvic aldehyde closely duplicates the spectra produced by solutions of exposed plastic. In general it appears that compounds containing an activated carbonyl group are formed during photo-oxidation of PMM and CAB, and that these compounds are primarily responsible for the color reactions with the diamines.

[1] The use of visible and ultraviolet spectroscopy to identify carbonyl compounds in photodegraded plastics, by V. E. Gray and J. R. Wright, Division of Organic Coatings and Plastics Chemistry (ACS) preprint (Apr. 1964).
[2] A colorimetric method for measuring polyester degradation due to weathering, by V. E. Gray and J. R. Wright, J. Appl. Polymer Sci. 7, No. 6, 2161 (Nov.–Dec. 1963). Also, Division of Organic Coatings and Plastics Chemistry (ACS) preprint (Apr. 1963).
For a brief treatment of this work, see Colorimetric determination of plastic degradation, NBS Tech. News Bull. 47, 64–65 (Apr. 1963).

exposed plastic and diamine. These spectra were then compared with those obtained from compounds that were possible oxidation products. Approximately half of 40 possibilities were eliminated because they produced no color upon reacting with a phenylenediamine, or because they produced absorbance peaks in a spec-

Book on *p*H Authored by NBS Chemist

A NEW BOOK, *Determination of* pH, *Theory and Practice,* has recently been written by Dr. R. G. Bates, Chief of the Electrochemical Analysis Section and Assistant Chief of the Analytical Chemistry Division. This book deals with the quantitative aspects of acidity in aqueous and nonaqueous solutions. It presents an authoritative treatment of the theory and nature of acidity, and emphasizes the scales and methods for measuring this property. The book also discusses in detail some possible approaches for establishing pH scales in mixed solvents and in nonaqueous media.

The present work (John Wiley & Sons, New York, $13) is an outgrowth of *Electrometric* pH *Determinations,* a book written by Dr. Bates a decade ago. Like the previous volume, the new book is chiefly concerned with theory and practice of electrometric *p*H measurements. Its scope is broader than that of the former treatise and includes a discussion of colorimetric *p*H determination with indicators. Significant developments of the past decade have also been included.

The first four chapters examine the definitions of *p*H scales, the conventions that permit acceptable compro-

mises between theory and experiment, and pH standards. A thorough exposition of the nature of the NBS standard scale is presented. The fifth and sixth chapters discuss buffer solutions and *p*H determinations by indicator methods from both the theoretical and the practical points of view.

Chapters 7 and 8 are devoted to acid-base phenomena and measurement scales in nonaqueous as well as in partly aqueous media. Chapter 9 describes the properties of hydrogen ion electrodes, liquid junctions, and reference electrodes. while chapter 10 reviews the properties and behavior of glass electrodes.

The final two chapters summarize the principles involved in measuring the electromotive force of *p*H cells. in constructing and operating *p*H meters, and in controlling *p*H. Because *p*H instrumentation has advanced so rapidly in the past decade. however. a broad coverage of the subject is beyond the scope of this book. These chapters, based on principles of measurement and instrumentation, are therefore written primarily for chemists rather than for engineers.

Publications of the National Bureau of Standards

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Technical News Bulletin, Volume **48**, No. 4, April 1964. 15 cents. Annual subscription: $1.50, 75 cents additional for foreign mailing. Available on a 1-, 2-, or 3-year subscription basis.

CRPL Ionospheric Predictions for July 1964. Three months in advance. Number 16, issued April 1964. 15 cents. Annual subscription: $1.50, 50 cents additional for foreign mailing. Available on a 1-, 2-, or 3-year subscription basis.

Journal of Research of the National Bureau of Standards

   Section A. Physics and Chemistry. Issued six times a year. Annual subscription: Domestic, $4; foreign, $4.75. Single copy, 70¢.

   Section B. Mathematics and Mathematical Physics. Issued quarterly. Annual subscription: Domestic, $2.25; foreign, $2.75. Single copy, 75¢.

   Section C. Engineering and Instrumentation. Issued quarterly. Annual subscription: Domestic, $2.25; foreign, $2.75. Single copy, 75¢.

   Section D. Radio Science. Issued monthly. Annual subscription: Domestic, $9; foreign, $11.50. Single copy, $1.

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   Commission 2. Tropospheric radio propagation.
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